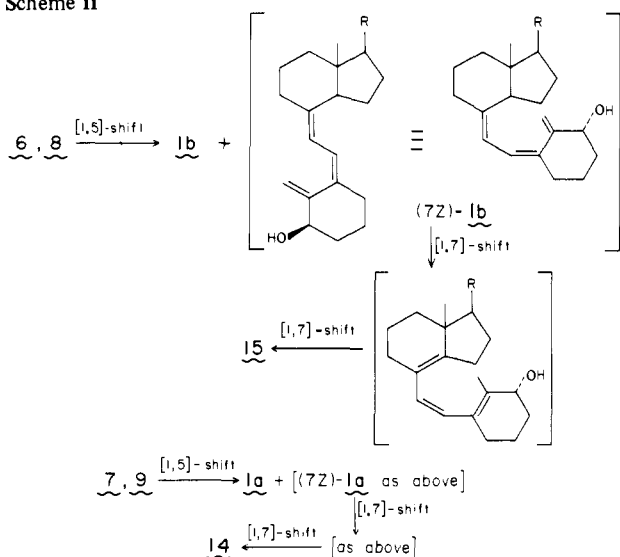


Scheme II



LiC≡CH (THF,  $-78\text{ }^{\circ}\text{C}$ , 90%)<sup>10</sup> and then Ac<sub>2</sub>O (C<sub>5</sub>H<sub>5</sub>N,  $\Delta$ , 36 h, 88%).<sup>11,12</sup> The coupling<sup>7</sup> of **5**<sup>13</sup> and **10b** followed by deprotection<sup>14b</sup> afforded a 37% yield of a mixture of **6** and **7**,<sup>14</sup> which was chromatographed to give pure **6** (10%, less polar) and **7** (12%, more polar).<sup>11,14</sup> Photolysis of **6** produced a 1:1 mixture of **6** and **8**; similarly **7** gave a 1:1 ratio of **7** and **9**.<sup>15</sup> These  $Z \rightleftharpoons E$  photoisomerizations proceed analogously to that observed for the known vinylallenes **12** and **13**.<sup>3</sup> Because **7**, **9** and **6**, **8** are convertible to **1a**<sup>5</sup> and **1b**, respectively (below), they are assigned the 1S and 1R configurations, respectively. The allene configurations are tentatively assigned on the basis of spectral comparisons (<sup>1</sup>H NMR, C-18 methyl) with **12** and **13**.<sup>3</sup> The C-18 methyl resonance of **6** or **7** ( $\tau$  9.34 for both) is similar to that of the 7R isomer **12** ( $\tau$  9.35); for **8**, **9**, and 7S isomer **13**, this same resonance appears at  $\tau$  9.29, 9.28, and 9.27, respectively. Thus, the coupling of vinyl cuprate **5** with **10b**, a formal S<sub>N</sub>2' process, occurs in a completely anti fashion. Certain dialkyl cuprate additions are known to exhibit similar anti selectivity,<sup>7b</sup> but exceptions are known.<sup>7</sup>

The allene **6** on thermolysis (refluxing isooctane, 8 h, N<sub>2</sub>) afforded a ~52% yield of **1b** as well as ~5% C and ~4% D. By contrast the C<sub>1</sub> epimer, **7**, gave only ~11% of the corresponding vitamin **1a**<sup>5</sup> accompanied by major amounts of A (~41%) and B (~23%).<sup>11</sup> There was essentially a reversal of product proportions when the photoisomers **8** and **9** were heated: **8** gave only ~9% **1b**, but ~45% C and ~18% D; **9** produced ~31% **1a**, ~4% A, and ~5% B.<sup>11,14</sup>

The four stereoisomers A–D possess similar spectral properties (UV, <sup>1</sup>H NMR) and are tentatively assigned as **14a**, **14b**, **15b**, and **15a**, respectively. The assigned intericyclic diene stereochemistry rests on the rational mechanistic pathway proposed in Scheme II. The major isomer (A or **14a** and C or **15b**) in each case from heating **7** and **8**, respectively, exhibited ~7-Hz bandwidths due to the C<sub>1</sub> proton in the NMR, while the minor isomers (B or **14b** and D or **15a**, respectively) exhibited larger bandwidths of ~23 Hz. The smaller bandwidth implies that the hydroxyl at C<sub>1</sub> and methyl at C<sub>10</sub> are trans diaxially related in **14a** and **15b**; the larger bandwidth (due to trans-C<sub>1,2</sub>-proton coupling) indicates that methyl and OH are cis in **14b** and **15a** with the methyl group fixed axially.<sup>16</sup> Since the C<sub>1</sub> configuration is presumably unchanged during the thermolysis, the C<sub>10</sub> configurational assignment follows.<sup>17</sup>

Our original synthesis of **1a** from cholesterol required 11 steps (0.2% overall yield).<sup>5</sup> The present convergent synthesis of **1a** involves 6–7 steps (0.7% overall yield from readily available vitamin D<sub>3</sub>); the epimer **1b** requires 6 steps (3% overall). The new vinylallene scheme, which will likely improve

on further exploratory studies, is made especially attractive by the fact that a host of A-ring fragments should be obtainable from the commonly available 2-methyl-1,3-cycloalkanediones.

**Acknowledgment.** We thank Dr. M. Rappoldt (Philips-Duphar, Weesp, the Netherlands) for a generous gift of vitamin D<sub>3</sub>. This investigation was supported by USPHS Grant No. AM-16595 from the National Institutes of Health. M.L.H. thanks the Graduate Division, University of California, Riverside, for a predoctoral fellowship. A.M. acknowledges the Spanish Ministry of Education and Science for partial postdoctoral support.

**Supplementary Material Available:** Spectral and analytical data (7 pages). Ordering information is given on any current masthead page.

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- (11) Absolute weighed yields are given except for the minor components (4–5%; based on UV calculations) produced on thermolyzing **6** and **9**.
- (12) The epimer **11b**<sup>9</sup> affords an apparently homogeneous alcohol different from **10a** and it is probably doubly epimeric to **10a** (C<sub>8</sub> and C<sub>14</sub>).
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- (14) The crude product consists of a relatively simple mixture of the desired vinylallenes, **10b**, and protonated **5** (by NMR). Prolonged reaction times or higher temperatures did not improve the yield of vinylallene. Two to three cycles of silica gel chromatography (67 × 1.5 cm column, 10–15% ether in 30–60 °C low boiling petroleum ether) effected separation of pure (TLC, NMR) **6** and **7** and the various isomeric **14**–**15** trienes. The isomers **6**–**9** and **14**–**15** exhibited no exceptional instability over many months (in ether under nitrogen, freezer).
- (15) Hanovia 100-W mercury arc, quartz, 5 × 10<sup>-3</sup> M (hexane), N<sub>2</sub>; purification according to note 14 (yield, 1:1 mixture, quantitative).
- (16) For the analogous 10,19-dihydrovitamins derived from vitamin D<sub>3</sub> (W. H. Okamura, M. L. Hammond, A. Rego, A. W. Norman, and R. M. Wing, *J. Org. Chem.*, **42**, 2284 (1977)), the C<sub>10</sub> methyl is forced into an axial orientation.
- (17) See A. Verloop, G. J. B. Corts, and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **79**, 164 (1960), for possibly analogous rearrangements involving *cis*-isotachysterol.

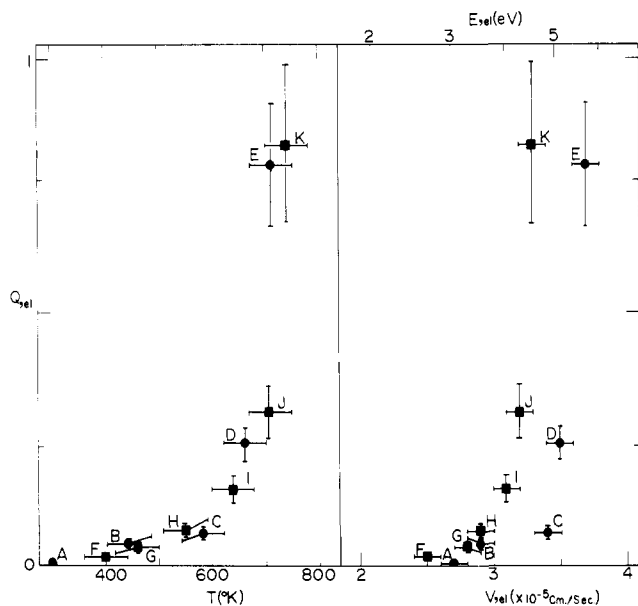
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Received February 6, 1978

## Crossed Molecular Beam Study of the Chemionization Reaction: SbF<sub>5</sub> + RX → SbF<sub>5</sub>X<sup>-</sup> + R<sup>+</sup>

Sir:

We report the title gas-phase chemionization reaction with RX = benzyl chloride, *tert*-butyl chloride (bromide, iodide), isobutyl iodide, isopropyl iodide, allyl bromide, bromoacetyl



**Figure 1.** Relative cross section  $Q$  vs. nozzle temperature and relative velocity for the reaction of benzyl chloride and  $\text{SbF}_5$ . The energy scale is calculated for the  $\text{SbF}_5$  monomer. ● ( $\text{H}_2$  carrier gas): A, 300 K; B, 443 K; C, 583 K; D, 663 K; E, 713 K. ■ (He carrier gas): F, 400 K; G, 460 K; H, 550 K; I, 640 K; J, 710 K; K, 740 K. In all cases the mole fraction of benzyl chloride was less than 1%.

bromide, benzoyl chloride, neopentyl chloride,  $\text{SF}_6$ ,  $\text{UF}_6$ . For the organic halides, with the possible exception of isobutyl iodide, only the parent peak ( $\text{R}^+$ ) was observed. Many groups<sup>1</sup> use the reaction between  $\text{SbF}_5$  and alkyl halides to generate carbonium ions in the liquid phase, where they can then be studied by temperature-dependent NMR. This is the first time that the above reaction has been used to produce gas-phase carbonium ions. Furthermore, the reaction seems to be quite general and could conceivably be used to generate cations from many more organic and inorganic halide containing compounds than we have studied.

The crossed molecular beam machine<sup>2</sup> consists of two nozzles, each mounted in a differentially pumped region such that the beams intersect, in the main vacuum chamber,  $90^\circ$  with respect to one another. The main vacuum chamber is pumped by a 10-in. oil diffusion pump which is mounted on the base. On the top of the chamber is a rotatable lid which supports a small separately pumped chamber housing a quadrupole mass filter and detector. A plate with a slight negative bias (ca.  $-3$  V) was mounted directly below the beam intersection region. Another plate, connected to a sensitive electrometer amplifier, was placed above the intersection region. Anions ( $\text{SbF}_5\text{X}^-$ ) formed from the reaction between  $\text{SbF}_5$  and  $\text{RX}$  were deflected by the negative potential to the upper plate, where the ion current was measured. A series of lenses for cation extraction were later added so that the  $\text{R}^+$  could be mass selected.

Both beams are seeded nozzle beams.<sup>2</sup> By varying the carrier gas and/or nozzle temperature we can independently vary the relative translational energy and the vibrational temperature of the beams. Our previous results,<sup>2</sup> on the dioxetane reaction, showed that the reactive cross section was a very sensitive function of the relative translational energy but was insensitive to the vibrational temperature. In contrast, the present results are very sensitive to vibrational temperature but insensitive to translational energy. On the right side of Figure 1 the relative reactive cross section  $Q$ , the ion current divided by the product of beam concentrations and the relative velocity, is plotted against the relative velocity. Both  $\text{H}_2$  and He were used as carrier gases. To achieve the same relative velocity using He as for  $\text{H}_2$ , a higher nozzle temperature is required for the He,

resulting in a higher vibrational temperature for the reactant.  $Q$  is much higher using He at the same relative velocity than it is using  $\text{H}_2$  because of the larger vibrational temperature in the case of He. On the left side of Figure 1  $Q$  is plotted vs. the nozzle temperatures of the seeded benzyl chloride beams. Here the results with He and  $\text{H}_2$  seeds are almost identical even though the relative velocities are quite different. We cannot rule out the possibility that  $Q$  drops to zero below the range in the translational energy covered. Even if this is true, we have shown that vibrational energy is important in the reaction and that translational and vibrational energies are *not* equivalent.

The data in the left side of Figure 1 could not be fit to the Arrhenius equation. There are two possible explanations: partial vibrational relaxation of the benzyl chloride during the beam expansion<sup>4</sup> and competing reactions involving both monomer and polymers of  $\text{SbF}_5$ . Further evidence of the second possibility is the behavior of  $Q$  vs. the vibrational temperature of the  $\text{SbF}_5$  beam. The chemionization cross section first increases slightly while the nozzle temperature is raised from 25 to 50  $^\circ\text{C}$ , then sharply decreases by an order of magnitude in the range of 50 to 100  $^\circ\text{C}$ , and leveling and remaining constant over the range of 100 to 350  $^\circ\text{C}$ . It is well known that gas phase  $\text{SbF}_5$  is associated even at temperatures as high as 400  $^\circ\text{C}$ .<sup>5</sup> A possible explanation of this behavior is that polymers of  $\text{SbF}_5$  are more reactive than the monomer, and, as the nozzle temperature is raised, the polymer concentration drops.

Anions were also detected in the reaction between  $\text{SbF}_5$  and  $\text{UF}_6$ . Here once again vibrational excitation in the reactant  $\text{UF}_6$  has a pronounced effect on the rate of reaction, but translational energy has little effect. There are several ways that this reaction could be used to separate isotopes. Multiphoton absorption of  $\text{UF}_6$  by a laser tuned to one isotope preferentially puts vibrational energy into that species giving it a vastly enhanced reactivity with  $\text{SbF}_5$ . The  $\text{UF}_5^+$  will be isotopically enriched. The reaction can also be used as a source of  $\text{UF}_5^+$  for subsequent mass selection by magnetic or ICR techniques. The rate of ionization is not limited by space charge as in a low-energy electron beam.

We have recently reconfigured the detector so that we can measure the distributions in product angle, kinetic energy, and mass, in order to obtain energy and angular contour maps which will give information on the detailed mechanism and the energy disposal of the reaction. Preliminary results for the reaction between  $\text{SbF}_5$  and benzoyl chloride indicates that a long-lived collision complex is formed. This would indicate the presence of a deep well in the potential-energy surface, involving an ion pair bound by a coulomb attraction with a dissociation energy of 2–3 eV. Since separated ions are seen, the system has sufficient energy to dissociate. Since vibrational and translational energies of activation are not equivalent, the activation barrier must lie before the well.

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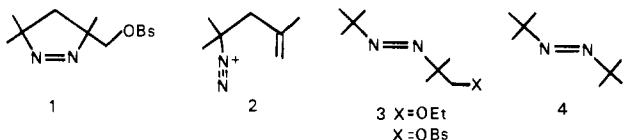
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### Evidence for a New Mode of Neighboring-Group Participation by the Azo Group

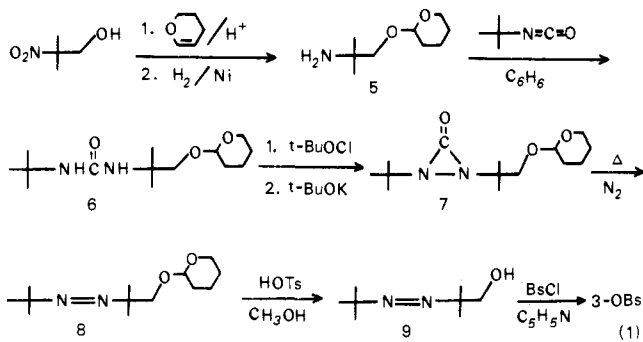
Sir:

During the last 8 years studies involving azo compound reactions have shown that the  $-N=N-$  group is one of the mechanistically most versatile functional groups in chemistry.<sup>1-9</sup> Cases of reaction by radical,<sup>2,3</sup> zwitterion,<sup>4</sup> carbene,<sup>5</sup> and cationic<sup>6</sup> mechanisms have been reported. Examples of concerted reaction pathways without formation of reactive intermediates<sup>7,8</sup> and reverse Diels-Alder processes<sup>9</sup> also have appeared.

One of our current research interests is concerned with the reaction of azo compounds by mechanisms which involve cationic intermediates. Recently we found that solvolysis of azo *p*-bromobenzenesulfonate **1** occurs with neighboring-group participation and elimination of nitrogen via diazonium-ion intermediate **2**.<sup>6a,b</sup> We now wish to report that solvolysis of **3-OBs** involves a new and entirely different kind of neighboring-group participation.



The synthetic sequence used to prepare **3-OBs** is outlined in eq 1.<sup>10</sup> The **5**  $\rightarrow$  **7** conversion is analogous to a reported diaziridinone synthesis.<sup>11</sup>



Azo *p*-bromobenzenesulfonate **3-OBs** was solvolyzed under anhydrous conditions in ethanol buffered with 2,6-lutidine. Rate measurements were made by the usual sealed ampule method. Titration of the developing *p*-bromobenzenesulfonic acid was performed using methyl red as the indicator.<sup>13</sup> Rates also were measured by <sup>1</sup>H NMR spectroscopy. All rate constants were nicely first order and the two methods gave essentially the same rate constant values. Some representative kinetic data are summarized in Table I. Reactivity comparisons of **3-OBs** with **3-OEt**, 2,2'-azobisisobutane (**4**),<sup>14</sup> neophyl *p*-bromobenzenesulfonate (**10a**), and neopentyl *p*-bromobenzenesulfonate (**10b**)<sup>15</sup> also are included.

Products derived from ethanolysis of **3-OBs** were found to vary with the amount of oxygen (air) present. Under oxygen-free reaction conditions<sup>16</sup> hydrazinium salt acetal **11** was the sole product detected.<sup>17,18</sup> On the other hand, excess air (O<sub>2</sub>)

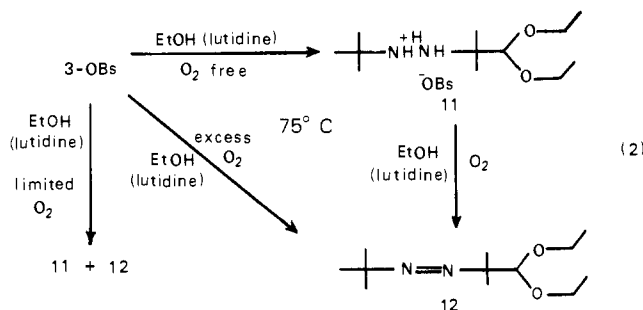
Table I. Ethanolysis Rate Data<sup>a</sup> and Reactivity Comparisons for **3-OBs**

compd	temp, °C	10 <sup>4</sup> k, s <sup>-1</sup>	rel rate
<b>3-OBs</b>	50.0	0.147 ± 0.01 <sup>b</sup>	2 × 10 <sup>7</sup> , 1 × 10 <sup>4</sup>
	74.9	1.64 ± 0.13 <sup>b</sup>	
	75	2.2 <sup>c</sup>	
<b>3-OEt</b>	184.4	2.66 ± 0.05 <sup>d</sup>	1
	159.8	0.181 ± 0.01 <sup>d</sup>	
	50.0	7.6 × 10 <sup>-9</sup> <sup>e</sup>	
<b>4</b>	184.7	2.81 ± 0.01 <sup>d</sup>	1
	185.0	2.51 ± 0.1 <sup>f</sup>	
	50.0	9.3 × 10 <sup>-9</sup> <sup>g</sup>	
	50.0	8.4 × 10 <sup>-3</sup> <sup>h</sup>	
<b>10a</b>	50.0	1.5 × 10 <sup>-5</sup> <sup>h</sup>	1 × 10 <sup>6</sup> , 5 × 10 <sup>2</sup>
<b>10b</b>	50.0	1.5 × 10 <sup>-5</sup> <sup>h</sup>	2 × 10 <sup>3</sup> , 1

<sup>a</sup> Dry EtOH with 0.010 M 2,6-lutidine and 0.005–0.008 M **3-OBs**.

<sup>b</sup> Titrametric rate. An aliquot of reaction solution was quenched with purified dioxane. The sample was then back-titrated with 0.011 M HClO<sub>4</sub> in dioxane using methyl red indicator.<sup>13</sup> <sup>c</sup> Measured in EtOH-*d*<sub>6</sub> (containing 0.1 M **3-OBs** and 0.2 M lutidine) by NMR integration of changes of reactant and product <sup>1</sup>H against the <sup>1</sup>H of 1,1,2,2-tetrachloroethane internal standard. <sup>d</sup> Liquid phase in EtOH in sealed Pyrex tubes which had been placed under N<sub>2</sub> by repeated freeze-pump-thaw cycles. The rate was obtained by monitoring the disappearance of the UV absorption at 370 nm. <sup>e</sup> Extrapolated from the higher temperature data. <sup>f</sup> Gas phase data.<sup>14</sup> <sup>g</sup> Extrapolated from gas phase data.<sup>14</sup> <sup>h</sup> Estimated from reported EtOH data using Δ*H*<sup>‡</sup> for AcOH.<sup>15</sup> The treatment also uses the well known approximation factor of 3 for *k*<sub>ROBs</sub> > *k*<sub>ROTs</sub>.

afforded only azo acetal **12**.<sup>17</sup> When solvolysis involved limited amounts of air, mixtures of **11** and **12** were obtained. A control experiment demonstrated the complete conversion of **11** to **12** in ethanol/air. These relationships are shown in eq 2.<sup>17</sup>



The reactivity comparisons in Table I are instructive. A near identity of reaction rates for **4** and reference compound **3-OEt** in ethanol makes it clear that the latter reacts by the usual free-radical process.<sup>2</sup> The exceptionally high reactivity ratio of 10<sup>7</sup> for **3-OBs** compared with **3-OEt** indicates reaction of **3-OBs** by some other kind of mechanism. This kinetic evidence is substantiated by the nature of the products observed (eq 2) and by the lack of nitrogen formation.<sup>17</sup>

These considerations and the titrametric method used to follow the reaction strongly suggest that ethanolysis of **3-OBs** involves some sort of cationic mechanism. Two plausible

